

**Title:** Light Hydrocarbon Gas Conversion Using Porphyrin Catalysts

**Authors:** Margaret C. Showalter, John A. Shelnut

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**Objective:**

The objective of this project is to develop novel catalysts for the direct conversion of natural gas to a liquid fuel. The current work investigates the use of biomimetic metalloporphyrins as catalysts for the partial oxidation of light alkanes to alcohols.

**Accomplishments and Conclusions:**

*Background.* Enzymes such as the cytochromes P450 are known to catalyze the partial oxidation of unactivated alkanes to alcohols. Analysis of these natural systems indicates structural features needed to create a biomimetic catalyst which will mimic the enzyme's high catalytic activity and selectivity. Metalloporphyrins have been reported to catalyze the oxidation of light alkanes to alcohols under mild conditions using molecular oxygen as the oxidant without the need for added co-reductant (Paulsen, D.R., Ullman, R., Soane, R.G., Closs, G.L., *J. Chem. Soc., Chem. Commun.* **1974**, 186. Ellis, Jr., P.E., Lyons, J.E., Symp. Oxygen Activation in Catalysis, ACS, April 22-27, 1990. European Patent Appl. No. 88304455.4, 1988). We are developing more active and selective catalysts for this process, toward the goal of obtaining a catalyst which is active enough to convert methane to methanol. We are using computer-aided molecular design (CAMD) in conjunction with activity testing to develop improved metalloporphyrin catalysts. Our stepwise approach to catalyst development involves first using CAMD techniques to design potential porphyrin catalysts, followed by the synthesis and characterization of promising catalysts, and finally subjecting these catalysts to bench scale activity testing. Catalyst testing experiments give insights into important structure-activity relationships which are used to evaluate and refine our modeling tools so that better catalysts can be developed.

In the previous year, we described a series of dodecaphenyl substituted iron porphyrin catalysts which had two desired structural features: 1) a substrate binding cavity and 2) a systematic variation of the redox potential of the Fe center caused by increasing numbers of fluorine substituents. We have found that placing large numbers of bulky substituent groups, such as phenyl groups, around the periphery of a porphyrin macrocycle causes a nonplanar distortion of the macrocycle which creates a rigid shallow cavity adjacent to the metal center. It

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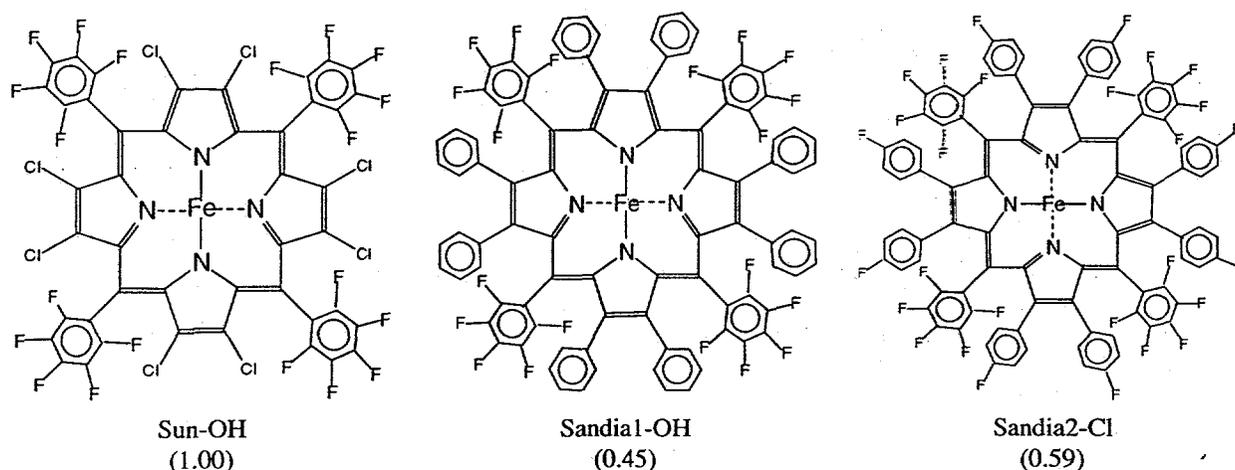
was predicted that this cavity would promote substrate binding and trap reactive intermediates adjacent to the metal center, although a deeper, more well defined cavity is required to fully realize these beneficial properties. This "micro-reactor" environment would thus improve catalyst activity and might also influence selectivity. We also predicted that highly substituted porphyrins such as our iron dodecaphenylporphyrin catalysts would have improved stability relative to traditional planar porphyrin catalysts because there is considerable steric hindrance to bifacial approach of two porphyrin molecules, thus inhibiting bimolecular catalyst destruction. Electron withdrawing groups were substituted on the phenyl rings of iron dodecaphenylporphyrin to create a series of catalysts,  $\text{FeF}_x\text{DPPCl}$  where  $x = 0, 20, 28, 36$ , with a range of overall electron depletion at the metal center. This catalyst series is unique because the bulky phenyl substituents create a nonplanar distortion leading to the formation of a cavity, as discussed above. In addition, these catalysts maintain this same shape across the series, even with the addition of fluorine substituents. In most other investigations of the effect of electron withdrawing substituents on metalloporphyrin catalyst activity, the addition of electron withdrawing groups to the porphyrin macrocycle has been accompanied by a change in the degree of porphyrin nonplanarity. Our unique catalyst series allowed us to study the effect of increased electron depletion of the metal center isolated from significant structural variation.

The  $\text{FeF}_x\text{DPPCl}$  catalyst series was tested in the oxidation of isopentane by molecular oxygen. For comparison, we also tested the commercial planar catalyst  $\text{FeF}_{20}\text{TPPCL}$ . This reaction was very selective for the production of alcohols. We observed the predicted trend -- catalytic activity increased with the degree of fluorination for the  $\text{FeF}_x\text{DPPCl}$  series. However, the overall activity of the  $\text{FeF}_x\text{DPP}$  catalysts was much lower than that of the planar catalyst,  $\text{FeF}_{20}\text{TPPCL}$ , despite the built-in cavity of the DPP catalysts. Furthermore, we observed that the porphyrins tested as oxidation catalysts degraded completely after several hours, even when the reactor was charged with a large amount of catalyst. Such rapid catalyst deactivation is in conflict with literature reports which indicate that metalloporphyrin catalysts in this type of reaction are stable for much longer time periods, some even for days (Ellis, P.E., Jr., Lyons, J.E., *Catal. Lett.* **1989**, 3, 389 and Lyons, J.E., Ellis, P.E., Jr., *Catal. Lett.* **1991**, 8, 45). Our catalysts were stable at the temperatures and pressures used in catalyst testing. Catalyst degradation was only observed in the presence of a reactive alkane substrate. This indicates that some species formed in the course of the oxidation reaction is responsible for the catalyst degradation. The short life of our catalysts, a problem in itself, also prevented us from making adequate comparisons for our designed catalysts. Although the amount of alcohol produced by  $\text{FeF}_{20}\text{DPPCl}$  was substantially less than the amount produced by  $\text{FeF}_{20}\text{TPPCL}$  under identical experimental conditions, we did not know if this was an indication that the DPP catalyst is less active, less stable, or a combination of both. One would expect similar activities and stabilities for the two catalysts based on the degree of electron depletion of the porphyrin by the substituents. (Charge depletion can be estimated from the sum of the Hammett  $\sigma$  constants of the substituents, and  $\text{FeF}_{20}\text{DPPCl}$  is predicted to be more active and stable or less active and stable depending on whether *meta* or *para* constants are used, respectively.)

Conclusions which can be drawn from our previous testing with the  $\text{FeF}_x\text{DPP}$  series are as follows: The importance of adding electron withdrawing substituents to alter the redox potential of the metal center was validated by the trend of increasing activity with increased degree of fluorination observed for this structurally homologous series. The catalysts were less stable than expected. However, if the reaction proceeds via a radical autooxidation mechanism,

this is not surprising. The concept of steric bulk preventing bimolecular catalyst destruction would be more applicable to a P450-like mechanism and to bulkier porphyrin catalysts than those investigated here. Any enhancement of the catalyst activity or selectivity by the cavity adjacent to the metal center was unable to be verified when O<sub>2</sub> is used as the oxidant. Rapid catalyst decomposition makes it impossible to definitively determine whether or not the pocket provides any beneficial effect. If it does, it is small enough to be canceled out by the poor stability and small differences in porphyrin charge depletion. In any case, molecular modeling suggests that a more enclosed cavity is required to achieve radical trapping, promote substrate binding, and prevent bimolecular degradation reactions.

**Current Progress.** Our previous attempts to measure the activity of Sandia-developed porphyrins as alkane oxidation catalysts have been hampered by rapid catalyst decomposition and low apparent activities. Furthermore, such low activities are inconsistent with results reported by other research groups, including scientists at Sun Co. At the invitation of Drs. James Lyons and Paul Ellis, Margaret Showalter traveled to the Sun Co. to test some of the Sandia catalysts in the Sun reactors. In this collaborative effort, two different Sandia porphyrins and one Sun porphyrin, shown in Figure 1, were tested side-by-side using a catalyst screening experiment developed at Sun for isobutane conversion. There are three major differences in the Sun procedure and the procedure used previously at Sandia. First, catalyst testing at Sandia has been performed in teflon-lined stainless steel reactors, while the reaction vessel employed at Sun is a glass aerosol tube. Second, the scientists at Sun have found that when the axial ligand coordinated to the metalloporphyrin is OH, the reaction is usually easier to initiate than when the ligand is Cl. Thus Sun prefers to screen potential catalysts as the OH form; however the porphyrins tested at Sandia have had Cl as the ligand. Before traveling to Sun, one of the Sandia catalysts to be tested was converted from the Cl-porphyrin to the OH-porphyrin. Finally, isopentane is the substrate used for screening at Sandia, since this alkane is a liquid and is thus simple to handle in the laboratory. However, the Sun researchers typically screen oxidation catalysts with isobutane as the substrate.



**Figure 1.** Structures of porphyrins tested at Sun Co.; -OH and -Cl indicate the axial ligand, not shown in the structure. The numbers in parenthesis are the predicted activities for identical axial ligands relative to the Sun-OH catalyst based on the sum of the Hammett para substituent constants).

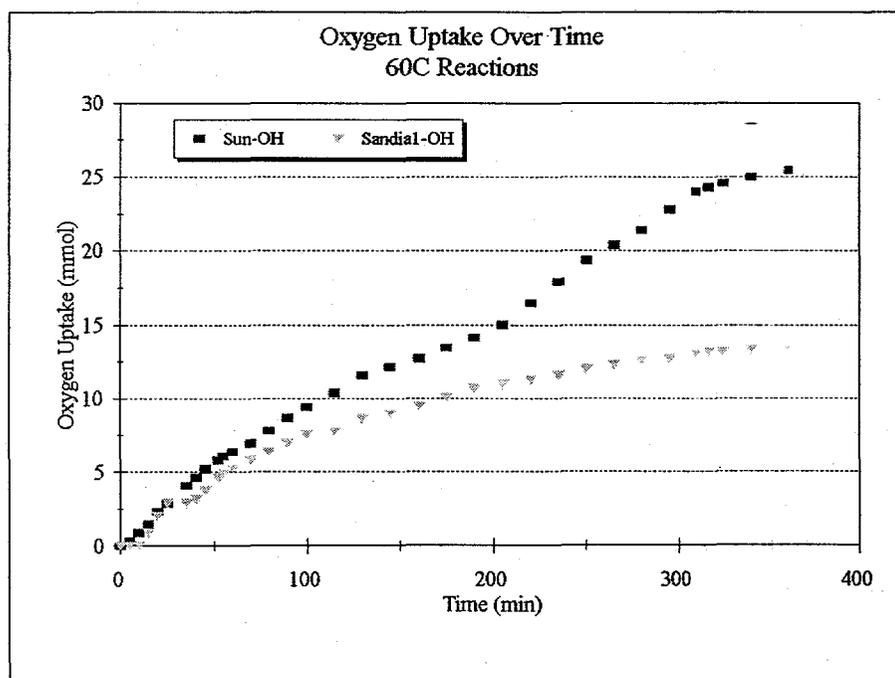
**Table 1. Summary of Reactions Performed at Sun Co.**

Catalyst ID	mmol catalyst	T (°C)	O <sub>2</sub> uptake (mmol)	Turnovers*	Visual observations
Sun-OH	0.013	60	25.4	1950	deep brown, constant color
Sandia1-OH	0.012	60	13.3	1100	initially dark red, lighter at 2.5 hr, continued lightening to reddish-orange
Sandia1-OH	0.017	80	14.5	850	initially dark red, lighter at 1hr, continued lightening to reddish-orange
Sandia2-Cl	0.013	80	0	0	no reaction, remained dark brown throughout

Reaction solutions contained catalyst and 7g isobutane in 25ml benzene. Solutions were heated while stirring for 6 hours under 100 psi of O<sub>2</sub>. \*Defined as mmol O<sub>2</sub> consumed /mmol catalyst.

Table 1 summarizes the experiments performed. The Sun-OH catalyst, which they had previously determined to be very active and robust, performed as expected. Oxygen uptake continued throughout the course of the reaction and no noticeable change in the deepness of color occurred. The Sandia1-OH catalyst performed well initially, taking up O<sub>2</sub> at a rate comparable to the Sun-OH catalyst. However, after a couple of hours, the Sandia1-OH solutions were noticeably lightened and oxygen consumption slowed. Eventually the solutions lightened to pale reddish-orange and O<sub>2</sub> uptake stopped. This lightening happened more quickly in the 80°C reaction. UV/Visible spectroscopy on the reacted Sandia1-OH samples indicated that there was

**Figure 2. Plot of oxygen consumption over time.**



no porphyrin left in these pale solutions. Thus, the turnovers achieved by the Sandia1-OH catalyst are lower because this porphyrin did not persist in the solution for the entire 6 hour run. Figure 2 shows O<sub>2</sub> uptake with time for the 60°C reactions, which gives a graphical indication of relative reactivity. Note that initially, the Sandia1-OH catalyst consumed oxygen at a rate comparable to the Sun-OH catalyst, but O<sub>2</sub> usage by the Sandia1-OH catalyst leveled off as the catalyst decomposed. Although the Sandia1-OH catalyst is not as stable as desired, this catalyst was more active and stable than previous experiments at Sandia using the Cl salt and isopentane had indicated.

GC was used to analyze the liquid products formed in these reactions. The only products formed in significant quantities were tertiary butyl alcohol (TBA, the desired product) and acetone, which results from cleavage of the isobutane substrate. The ratio of TBA to acetone is 9:1, thus the selectivity for the desired product is excellent. Approximately 90% of the measured oxygen uptake can be accounted for by these two products.

The Sandia2-Cl catalyst was unreactive, even though the higher temperature of 80°C was used for this compound. This lack of reactivity is consistent with previous observations at Sun that iron porphyrin chlorides are often difficult to initiate. Catalyst testing to date at Sandia has been done with Cl porphyrins, and this warrants change. However, the problem we had had at Sandia was not that the porphyrin did not react at all, but rather that once the reaction was initiated, the porphyrin was short-lived. We had also found that temperatures of 100°C were required. This higher temperature is high enough to cause the relatively unreactive Cl to react, but catalyst decomposition is probably also accelerated by this higher temperature. High activities for the Cl catalysts previously reported by Sun are probably the result of incomplete conversion to the chloride form.

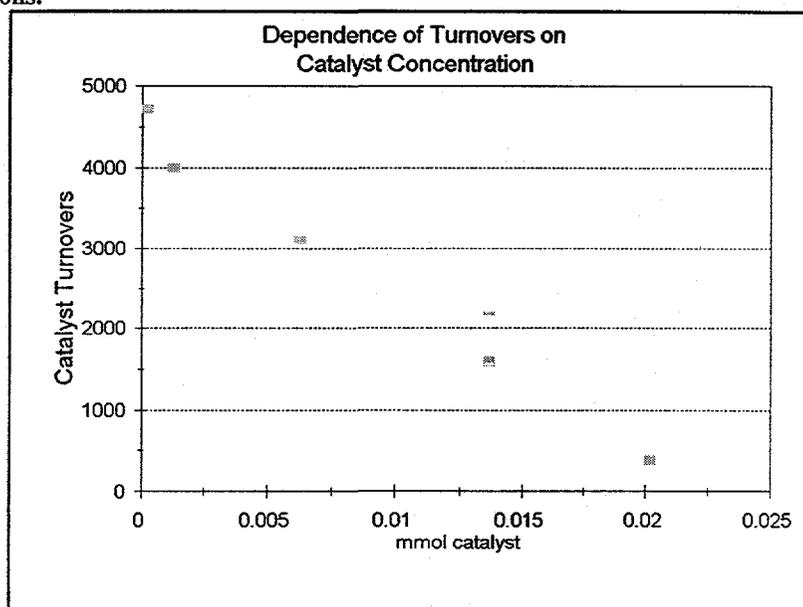
In summary, the initial activity of the Sandia1-OH catalyst was comparable to that of Sun-OH, one of Sun's best catalysts; however the Sandia material is not as robust (as predicted on the basis of the Hammett constants, see Table 1). The measured activity of the Sandia1-OH catalyst was significantly higher as tested at Sun than in previous experiments at Sandia. The Sandia2-Cl catalyst was completely unreactive under the mild conditions used. In the future, axial Cl should be avoided to facilitate easier catalyst screening; conversion to the azide or hydroxide complex will be used to promote catalysis. The glass-tube reactors utilized at Sun provide a quick, easy, reliable method for screening oxidation catalysts, and have the added advantage of allowing visual observation of the reaction in progress.

Since the visit to Sun, we have constructed a glass tube reactor in our laboratory at Sandia which is essentially identical to those used at Sun. We also added an additional pressure gauge to the teflon lined steel reactors, so that we can more accurately monitor and control the pressure. In an attempt to apply some of the insights gleaned from the collaborative work with Sun, we passed commercial FeF<sub>20</sub>TPPCl through a column of activated alumina to exchange the axial Cl ligand. (The material obtained from the column is a mixture of hydroxide and  $\mu$ -oxo dimer). We then used this porphyrin to catalyze the oxidation of isopentane. However, we found that even with the non-Cl porphyrin, a temperature of 100°C was needed for the reaction to proceed, and the catalyst was consumed quickly at this temperature. When isobutane was used as the substrate, the reaction proceeded at 80°C, catalyst decomposition was minimal, and turnovers comparable to those reported by Sun were obtained. Thus it appears that the choice of alkane substrate is as important as the axial ligand of the catalyst in obtaining results consistent with those published by Sun. The lower activity with isopentane than with isobutane is unexpected

and this result needs to be understood. Also, there does not appear to be any inherent problem with the teflon reactors, as we once believed. We can get excellent catalytic turnovers with minimal catalyst degradation in these reactors when isobutane is used as the substrate and the axial ligand of the porphyrin is not Cl.

An interesting facet of this chemistry is that the catalyst turnovers (amount of oxygenated products/amount of catalyst) are dependent on the initial catalyst concentration, as shown in Figure 3. Such a phenomenon may indicate that true catalytic rates can not be determined under these experimental conditions. In fact, for the higher catalyst concentrations plotted in Figure 3, the amount of oxygenated products produced was essentially the same. Thus a doubling of catalyst concentration leads to a halving of the turnovers calculated. To obtain true catalytic activities we need to be operating under conditions for which doubling the amount of catalyst doubles the product produced. Therefore, it is critical to be very careful when comparing catalysts which have not been tested under identical conditions.

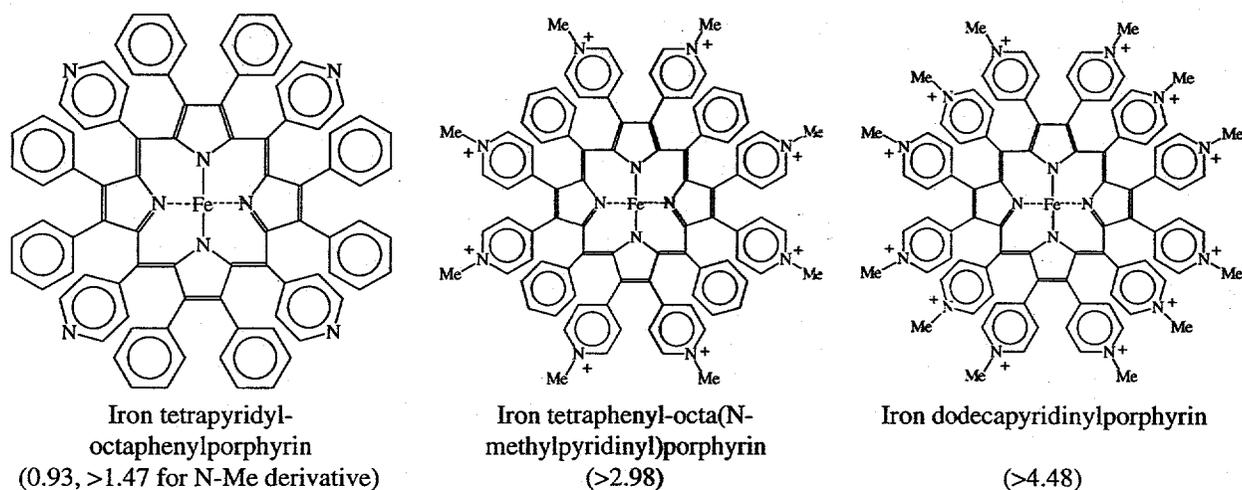
**Figure 3.** Plot of catalyst turnovers vs. amount of catalyst for a series of FeF<sub>20</sub>TPP catalyzed isobutane reactions.



Synthesis has begun on a new class of highly substituted metalloporphyrin catalysts. These new catalysts are also based on the parent iron dodecaphenylporphyrin (FeDPP). However, we are pursuing a different route to charge deplete the porphyrin ring. Synthesis of porphyrins becomes problematical when highly electron withdrawing substituents are present. Therefore, we have devised a method of assembling the porphyrin macrocycle with less electron-withdrawing substituents (pyridyl) and then converting the substituents to highly electron withdrawing ones (pyridinyl). In order to improve the catalyst stability and activity, in the new class of dodeca-substituted iron porphyrins some or all of the phenyl rings are replaced by pyridyl or pyridinyl groups. Representative catalysts of this type are shown in Figure 4, along with their activity number relative to Sun-OH (Figure 1). Quaternizing the N of the substituent pyridyl groups greatly enhances the electron withdrawing effect on the Fe center. The Hammett constant for phenyl, perfluorophenyl, 4-pyridyl, and 4-pyridinyl groups are -0.01, 0.41, 0.83, and >1.30,

respectively. Furthermore, these ionic groups provide a site for anchoring the catalyst molecules to an inorganic support such as silica and alumina, thus enhancing catalyst stability and providing a means for easy recovery of the catalyst.

Activity testing of these pyridyl porphyrins requires changing our experimental protocol. These cationic porphyrins will not be soluble in the benzene currently used for homogeneous testing experiments, so they will first be applied to an inorganic support. We are currently developing suitable procedures for preparing and testing such a heterogeneous catalyst using the commercially available iron(III) chloride tetra(N-methyl-4-pyridinyl)porphyrin tetratosylate (predicted activity relative to Sun-OH: 1.49) supported on silica. Preliminary tests show this supported catalyst to be active under the same conditions as the homogeneous catalysts. This is the first demonstration that this supported catalyst is active when O<sub>2</sub> is used as oxidant. This shift from homogeneous to heterogeneous catalysis is significant because heterogeneous catalysts are likely to be better suited to the conversion of a gaseous substrate in flow reactors. We anticipate that this new class of porphyrins will also exhibit enhanced activity and stability.



**Figure 4.** Pyridyl and N-methyl pyridinyl porphyrins based on parent dodecaphenylporphyrin structure. Counter ions are not shown. (Predicted activities relative to Sun-OH catalyst in Figure 1.)

In addition to the synthesis of these new catalysts, we are also making progress in the synthesis of more stable and active porphyrins in the fluorinated dodecaphenyl series. The most fluorinated of this series tested to date is F<sub>36</sub>. However, recent progress in synthesis using the Susuki reaction may soon yield F<sub>40</sub>DPP and F<sub>60</sub>DPP. The fully fluorinated F<sub>60</sub> material will be particularly interesting to test since all possible H's in the parent FeDPP will be replaced by F. It is possible that part of the instability of the previously tested catalysts in the FeDPP series is due to the presence of CH bonds on the substituent groups which are susceptible to attack by radical intermediates. The F<sub>60</sub>DPP catalyst, in addition to being the most electron deficient of the series, will not have any CH bonds.

Molecular design studies are underway to engineer catalyst with deeper cavities that are easily synthesizable. These catalysts are also based on the dodeca-substituted porphyrins, including the 2- and 3-pyridinyl analogs of the catalysts shown in Figure 4.

**Plans:**

We will continue the development of an experimental protocol for testing the catalytic activity of supported porphyrin catalysts using a heterogeneous material prepared from a commercial tetrapyrrolyl porphyrin. Once we have demonstrated the ability to reproducibly prepare and test the supported catalyst, we will be ready to test the new pyridyl porphyrins that are currently being synthesized. We anticipate having several of these new porphyrins available for testing before the end of this report period.

Once the additional fluorinated DPP catalysts, F<sub>40</sub>DPP and F<sub>60</sub>DPP, become available, we will test these materials using the optimized homogeneous process discussed in this paper. These materials may also be available in testable quantities this summer.

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